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PART III

INVESTIGATION OF CATALYTIC REACTIONS FOR CO$_2$ REDUCTION

PART III. EVALUATION OF PRECIOUS METAL CATALYSTS

EDWARD B. THOMPSON, JR.

TECHNICAL REPORT FDL-TDR-64-22, PART III

OCTOBER 1965

AIR FORCE FLIGHT DYNAMICS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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INVESTIGATION OF CATALYTIC REACTIONS
FOR CO$_2$ REDUCTION

PART III. EVALUATION OF PRECIOUS METAL CATALYSTS

EDWARD B. THOMPSON, JR.

FOREWORD

This report covers work conducted as Phase 3 of an in-house research effort concerning the investigation of catalysts for the reduction of carbon dioxide for space vehicle atmospheric control. This effort is being conducted by the Air Force Flight Dynamics Laboratory of the Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was initiated under Project No. 6146, "Atmosphere and Thermal Control," Task No. 614612, "Oxygen Recovery from Carbon Dioxide." The chief investigator is Mr. E. B. Thompson, Jr., with assistance from Messrs. A. Civetz and K. Wess. The third phase of this continuing program was initiated in May 1964 and completed in November 1964. The manuscript was released by the author in July 1965 for publication as an RTD Technical Report. Since this is a continuing program, this report is designated Part III.

Publication of this technical report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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ABSTRACT

The precious metals of ruthenium, rhodium, and iridum were selected as the final group of catalyzing materials to be experimentally evaluated for effectiveness in promoting the catalytic reduction of carbon dioxide by hydrogen to methane and water. A catalytic reactor having a length to diameter ratio of 18 was designed, fabricated, and utilized for the experimental evaluation of these catalysts. The reactor processed 2.2 pounds of CO_2 per day, equivalent to a one-man daily output. The minimum temperature required to achieve the maximum CO_2 conversion rate of 99 percent was 450°F and this occurred for the ruthenium catalyst. Conversion rates of 99 and 67 percent were obtained with the rhodium and iridium catalysts at temperatures of 704° and 892°F, respectively. The 99 percent conversion rate for ruthenium held for the temperature range of 450° to 650°F. All reactions took place at 1 atmosphere pressure. The total weight of hydrogen required to reduce the 2.20 pounds of CO_2 under these conditions is 0.39 pounds. Each of the three catalysts had reactor batch weights of approximately 253 to 258 grams. After completion of each experimental run at the pre-set temperature, the catalyst was examined for possible carbon deposition and physical deterioration. No evidence of either condition was noted for ruthenium and rhodium; the iridium catalyst, however, had been partially reduced at the higher experimental reaction temperatures. The report introduces discussions of the effect of quantitative factors such as catalyst particle size and shape on reaction yield.

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INTRODUCTION

PROGRAM OBJECTIVES

This report summarizes the work conducted as the third phase of a continuing in-house research program concerning the Sabatier methanation reaction or the reduction of carbon dioxide by hydrogen catalysis. The completion of this third phase marks the end of the qualitative investigative work to be performed during this in-house program.

The scope of phases 1, 2, and 3 encompassed the two-fold objective of, first, determining a practical technique for an experimental evaluation of Sabatier reaction catalysts and, second, pinpointing that catalyst or family of catalysts which would be most effective in promoting this reaction to maximum water yield and at minimum temperature conditions.

The general approach taken during phase 1 was to evaluate the effectiveness of a nickel-kieselguhr catalyst for promoting the Sabatier methanation reaction. The experimental evaluation provided data which served to identify and correlate the physicochemical properties of this catalyst with its ability to promote the reaction. This information was reported in FDL-TDR-64-22, Part I, which served as a base line for evaluating additional catalysts during phases 2 and 3. The phase 2 work consisted of experimentally evaluating additional base metal catalysts such as molybdenum, cobalt and copper. This work was reported in FDL-TDR-64-22, Part II with the results showing that next to the nickel-kieselguhr catalyst cobalt on an aluminum oxide substrate was the most effective methanation catalyst at low temperature. The remaining catalysts of interest, the precious or noble metals of ruthenium, rhodium, and iridium, were then experimentally evaluated during phase 3, and are discussed in this report.

Future work to be conducted as part of this in-house effort will consist of determining the quantitative properties of the catalysts qualitatively selected during phases 1, 2, and 3. The size, shape, volume, and reactor batch weights will be determined for each catalyst as well as the quantitative relationship of each catalyst to the size and configuration of the catalytic reactor. This work will be conducted as phase 4 of this continuing program.

The particular catalysts selected for experimental evaluation and considered most feasible for promoting the Sabatier reaction must satisfy the following general conditions:

(a) The physicochemical properties of the catalyst must be identifiable for correlation with its effectiveness in promoting the reaction.

(b) The catalyst must be capable of initiating and sustaining the reaction at a temperature of 300°F and a pressure of 1 atmosphere.

(c) The catalyst must be capable of sustaining the reaction at maximum CO_2 conversion at the reaction conditions specified in (b) above.

(d)   The catalyst must be resistant to "poisoning" by sulfur compounds, halogen com-
pounds, etc., or be easily regenerable by heating and/or purging with hydrogen.

(e)   The catalytic reactor containing the catalyst in question must be capable of converting
a minimum of 2.20 pounds of CO_2 per day to water and methane.

SECTION II

ANALYTICAL PROGRAM

The "Theory of Catalysis" and "Techniques of Catalyst Preparation" are discussed in FDL-TDR-64-22, Part I.

ANALYSIS OF THE PRECIOUS METAL CATALYST

General Description

The precious metal elements listed in group VIII of the periodic table were surveyed for their probable applicability as methanization catalysts. The three catalysts selected from the literature survey for the phase 3 investigation consisted of ruthenium, rhodium and iridium on alumina (see Figures 1, 2, and 3).
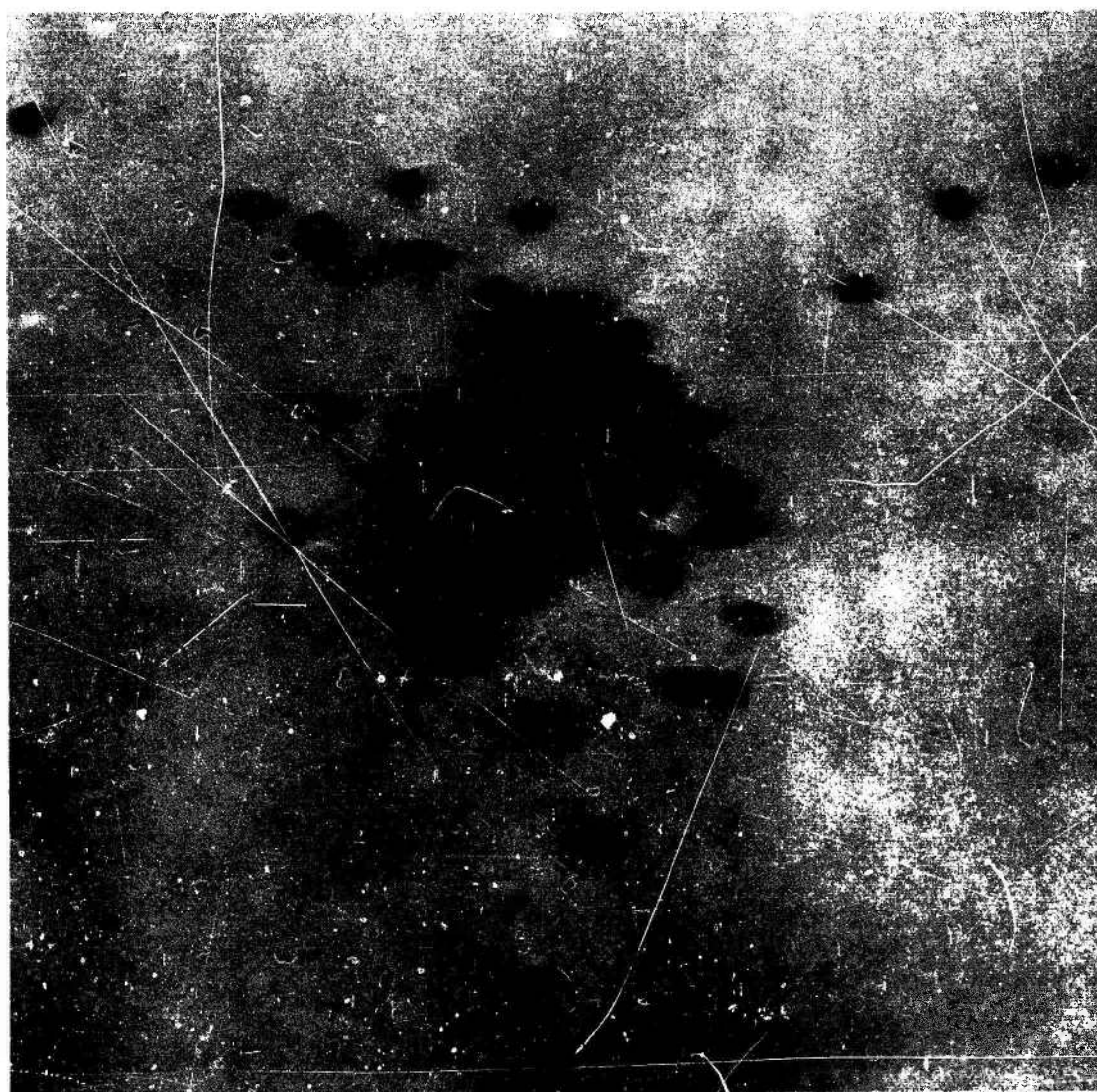
Figure 1. Ruthenium Catalyst Pellets

Figure 2. Rhodium Catalyst Pellets

Figure 3.   Iridium Catalyst Pellets

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The metals are the catalyzing coatings while the alumina or aluminum oxide acts as the carrier. The aluminum oxide carrier comprises 99.5 percent of the mass and provides a large internal surface area because of its skeletal structure.

The three catalyst reactor batch loadings for rhodium, ruthenium and iridium were 257.5 g, 244.8 g, and 252.6 g, respectively. Each batch loading represents that quantity of catalyst required to fill the reactor.

CATALYST PROPERTIES

Densities

The three densities which were of value during this experimental program and which were experimentally determined are the bulk density, B, mass per unit volume of catalyst bed; the particle density, P, mass per unit volume of particle; and the solid density, C, mass per unit volume of solid free from all voids, external and internal. The density values determined for the three catalysts are shown in Table I.

TABLE I

CATALYST DENSITIES (g/cc)

	B	P	C
Ruthenium	1.95	2.50	7.80
Rhodium	1.98	2.54	7.93
Iridium	2.14	2.75	8.56

The external void fractions of the catalysts bed are determined by the following relationships:

$$F_{e_{Ru}} = 1 - \frac{B}{P} = 0.22$$

$$F_{e_{Rh}} = 1 - \frac{B}{P} = 0.22$$

$$F_{e_{Ir}} = 1 - \frac{B}{P} = 0.22$$

The internal void fractions of the catalysts beds are determined by the following relationships:

$$F_{i_{Ru}} = 1 - \frac{P}{C} = 0.68$$

$$F_{i_{Rh}} = 1 - \frac{P}{C} = 0.68$$

$$F_{i_{Ir}} = 1 - \frac{P}{C} = 0.68$$

Surface Area

The total surface area available from each of the three catalysts can be calculated from the following general relationships:

$$A_T = A_E - A_I$$

where

A_T = total area in cm^2

A_E = external gross area in cm^2

A_I = internal area in cm^2

Calculating A_E from:

A_E = area per particle x particles per gram x number of grams

$$A_{E_{Ru}} = 0.330 \ \frac{cm^2}{particle} \ x \ \frac{20 \ particles}{grams} \ x \ 258 \ grams = 1705 \ cm^2$$

$$A_{E_{Rh}} = 0.330 \ \frac{cm^2}{particle} \ x \ \frac{20 \ particles}{grams} \ x \ 245 \ grams = 1620 \ cm^2$$

$$A_{E_{Ir}} = 0.330 \ \frac{cm^2}{particle} \ x \ \frac{18 \ particles}{grams} \ x \ 253 \ grams = 1504 \ cm^2$$

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Calculating A_I from:

$$V_O = V_T - V_S$$

where

V_O = volume of open space, internal plus external

V_T = total volume occupied by weight of catalyst material

V_S = volume of solid material

$V_{S_{Ru}}$ = 258 grams $\times \dfrac{1 \text{ cc}}{7.80 \text{ grams}}$ = 33 cc

$V_{S_{Rh}}$ = 245 grams $\times \dfrac{1 \text{ cc}}{7.93 \text{ grams}}$ = 31 cc

$V_{S_{Ir}}$ = 253 grams $\times \dfrac{1 \text{ cc}}{8.56 \text{ grams}}$ = 29 cc

So

$V_{O_{Ru}}$ = 232 - 33 = 199 cc

$V_{O_{Rh}}$ = 232 - 31 = 201 cc

$V_{O_{Ir}}$ = 232 - 29 = 203 cc

Effective Particle Size

The effective particle sizes for the three catalysts can be calculated from the relationship:

$$D_P' = \frac{6V_P}{A_P} = \frac{6 (1 - Fe)}{A_V} = \frac{6}{A_m \rho P}$$

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where

V_P = average volume per particle

A_P = average gross exterior area per particle

F_e = fraction external void volume

A_V = surface area of particles per unit volume of bed

A_m = surface area per unit mass of particles

ρ_P = density of particles mass unit per volume

So

$$D_P' = \frac{6V_P}{A_P} = \frac{6\,(0.026)}{(0.482)} = 0.324 \ \text{centimeters}$$

Effectiveness Factor

It is evident from the discussion of internal and external void fractions that in a fluid reaction catalyzed by a porous solid the concentration of the fluid reactant at the interface will be lower at the interior surfaces than at the gross external surface of the particle and that the rate of reaction per unit interfacial area will be lower at the interior surface. This is also recognized from the calculations on total available area of the catalyst where the gross exterior area is a small fraction of the total area. The ratio of the actual rate of reaction per unit mass of solid to the rate which would exist if the concentration at all interior interfaces were the same as those at the gross exterior surface has been termed the effectiveness factor of the catalyst. The general equation for the rate of a reaction catalyzed by a porous solid is as follows:

$$\gamma\Delta = C\Delta_{a_i} = E_A \, J\Delta_{a_i}$$

where

$\gamma\Delta$ = reaction rate per unit mass

C = observed overall rate factor of the reaction

Δa_i = driving force of the reaction in terms of activities at the external surface of the particle

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E_A = effectiveness factor

J = the rate factor of the catalytic reaction which when multiplied by the driving force Δa_i gives the rate of reaction per unit mass of catalyst if the driving force is uniform throughout

An effectiveness factor of 1.0 indicates that the reaction rate at all interior surfaces is the same as that at the exterior surfaces. This is particularly true when (1) the particle size is small, (2) the pores are large and well interconnected, (3) the rate factor of the reaction is relatively low, and (4) the diffusion coefficients of reactants and products are high. It has been proven for reactions in which the rate is proportional to the first power of the concentration at the interface. The effectiveness factor is a function of a modulus which is defined as follows:

$$M = \frac{D'P}{2} \sqrt{\frac{K}{cD_v}}$$

where

M = Thiele's Modulus

$D'P$ = effective particle diameter

c = average radius of pores in the particle

D_v = diffusion coefficient

K = reaction velocity constant

The modulus may also be expressed in the form:

$$M = \frac{D'p \, a' \, e^{\frac{b'}{T}}}{F_i \cdot /4}$$

where a' and b' are empirical constants, characteristic of the reaction process and F_i is the internal void fraction.

By calculating the modulus for a number of temperature values it is possible to determine the effectiveness factor for the catalyst from standard reference graphs depicting effectiveness factor vs. Thiele's Modulus.

Since the ruthenium on alumina catalyst proved to be the most effective of the three investigated, it was decided to calculate the effectiveness factor of this catalyst for a 1/8 in. pellet size.

In order to calculate the effectiveness factor, an identical ruthenium catalyst of 1/4 in. pellet size was also evaluated in the reactor at the maximum yield temperature of 450°F. Conversion to the English system of units was adopted for ease in use of the modulus equation. An alternate temperature of 550°F was selected for the second run with both catalysts in order to obtain the necessary data for solving the problem.

The following data was recorded for the purpose of calculation:

Catalyst Size	1/8 in.	1/4 in.
Pellet diameter, D'_P, ft	0.0104	0.0208
Pellet density, $_P$, lbs/cu ft	156	156
Solid density, P_c, lbs/cu ft	486	486
Temperature, °C	232	232
T, lb-moles/(lb)(hr)	0.0405	0 0.0710
Temperature °C	288	288
T, lb-moles/(lb)(hr)	0.046	0.075

Calculating the effectiveness factor of the 1/8 in. pellet size catalyst having a 68 percent interval void fraction at a temperature of 232°C:

Catalyst Size	1/8 in.	1/4 in.
Pellet area, sq in.	0.075	0.446
Pellet volume, cu in.	0.0001	0.0125
D'_P, ft.	0.0107	0.0214
F_i	0.68	0.68
$(F_i)^{1/4}$	0.91	0.91
$D'_P/(F_i)^{1/4}$	0.0118	0.0235
Temperature, °C	232	288
$E_A 1/E_A 2 = r_1/r_2$	0.570	0.605

$$\frac{M_T 1}{M_T 2} = \frac{(D'_{P1})(F_i 2)^{\frac{1}{4}}}{(D'_{P2})(F_i 1)^{\frac{1}{4}}} = 0.5 \qquad\qquad 0.5$$

$M_T 1^*$	10.0	7.0
$M_T 2^*$	5.0	3.5
$E_A 1^*$	0.27	0.36
$E_A 2^*$	0.48	0.60

Substituting in the modulus equation for catalyst size 1/8 in., gives:

$$\log 10 = \log a' + \log 0.0118 + \frac{b'}{(2.303)(505)}$$

$$\log 7 = \log a' + \log 0.0118 + \frac{b'}{(2.303)(561)}$$

$$a' = 8.0 \quad b' = 1010$$

then:

$$D' = 0.0107 \text{ ft} \quad \frac{D'}{4F_i} = \frac{0.0107}{4 \quad 0.68} = 0.0118$$

$$M_T = D' \, a'_e \, \frac{b'}{T} = \frac{(8.0)(0.0107) \, e^{\frac{1010}{505} = 0.651}}{(0.91)}$$

$$E_A = 0.96^*$$

An effectiveness factor of 0.96 indicates that 0.5 percent ruthenium (on alumina) catalyzes the reduction of carbon dioxide at a temperature of 450°F to nearly 100 percent conversion. This was demonstrated to be the case during the experimental program.

*Hougen, O. A., and Watson, K. M., Chemical Process Principles, Part 3, Kinetics and Catalysis, Figures 195 and 196, John Wiley & Sons, Inc., 1949.

CO_2 REDUCTION REACTIONS AND EQUILIBRIUM

All carbon dioxide reduction reactions and specifically the Sabatier reaction, behave as any other chemical reaction in that when hydrogen and carbon dioxide react with each other to yield water and methane, the reaction will proceed until each of the initial reactants has decreased to a certain concentration and each of the products formed has increased from zero to a certain concentration. This phenomenon occurs for all chemical reactions if a sufficient length of time for a specific batch of reactants is allowed; however, the length of time varies greatly from one reaction to another. (This time is usually referred to as "space velocity" when a continuous process is involved.*) It also holds true for a continuous-flow process in which the space velocity is relatively low. The Sabatier reaction is stoichiometrically represented as follows:

$$4H_2 + CO_2 = CH_4 + 2H_2O$$
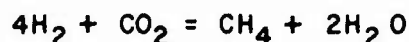
The concentrations of the reactants and products at this point are referred to as equilibrium concentrations, and gases reacting to form other gases may be measured as percentages by volume. These volume percentages are mathematically related to each other in a definite manner which is dependent upon the chemical equation written for the reaction, and upon a constant, K, which is determined from the thermodynamic properties of the initial components and final products. For example, the general form equation which can be written for any CO_2 reduction reaction is

$$(3n + 1) \ H_2 + nCO_2 = C_nH_{4n} + 2nH_2O$$
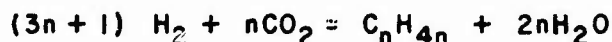
where N = 1 for the Sabatier reaction, or

$$4 \ H_2 + CO_2 = CH_4 + 2H_2O$$

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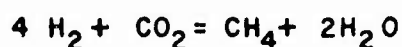
*Space velocity is defined as the volume of feed measured at standard conditions per unit time per unit volume of reactor.

The equilibrium equation relating gas volume percentages, represented by the term "x," with representing reaction total pressure, is

$$K = \frac{\left(^xH_2O\right)^2 \left(^xCH_4\right)}{\left(^xCO_2\right)\left(^xH_2\right) 4} (2+1) - (1+4)$$

$$K = \frac{\left(^xH_2O\right)^2 \left(^xCH_4\right)}{\left(^xCO_2\right) \left(^xH_a\right) 4}$$

The equilibrium constant, K, is related to the Gibb's free energy change in the standard state, G°, according to the following formula:

$$-\frac{G^0}{T} = R \ln K$$

where T is the reaction temperature, and R is the universal gas constant. The quantity $\frac{G^0}{T}$ may be evaluated from the following:

$$\frac{G^0}{T_T} = \left(\frac{G^0_T - H^0_0}{T} + \frac{H^0_{fo}}{T}\right)_{Prod.} \left(\frac{G^0_T - H^0_0}{T} + \frac{H^0_{fo}}{T}\right)_{React.}$$

where,

G^o_T = standard Gibbs' free energy at temperature T

H^o = enthalpy of the compound or element at 0°K

H^o_{fo} = standard heat of formation at 0°K

$G^{\circ}_T - H^{\circ}/T$		H°_{fo}
(cal) / (g-mole) (°K)		(cal) / (g-mole)
CO_2	-51.060	-94,052
H_2	-31.204	-0.0
H_2O	-45.106	-57,798
CH_4	-44.500	-17,889

SECTION III

EXPERIMENTAL PROGRAM

GENERAL PLAN

The experimental program consisted of experimentally evaluating three precious metal catalysts to determine which would be the most effective for catalyzing the reduction of CO_2 with hydrogen to a maximum water yield at minimum temperature. The accomplishment of this objective was intended to provide a laboratory procedure for evaluating the effectiveness of all such catalysts considered as a possibility for effecting this reaction.

A standard laboratory evaluation plan nearly identical to that used in phases 1 and 2 was adopted. A catalytic reactor having a length to diameter ratio of 18 was designed and fabricated (see Figure 4). Precious metal catalysts of rhodium, ruthenium, and iridium mounted on an aluminum oxide (AL_2O_3) substrate were procured for experimental evaluation. The catalysts were subjected to a single variable of 12 different temperatures to which the catalytic reactor had been preheated before the introduction of the carbon dioxide and hydrogen gases. All other factors which could affect the reaction such as pressure, flow rate, and hydrogen to CO_2 volumetric ratio were held constant. The experimental plan consisted of determining the yield of water of 12 different reaction temperatures for each of the three catalysts.

The fundamental theory of catalysts and, particularly, for this reaction, discussed in Part I of FDL-TR-64-22, served as the criteria for determining the catalyst bed temperature range to be used in this phase of the experimental plan.

APPARATUS

The catalytic reactor and accessory equipment was arranged as CO_2 reduction system as depicted in Figures 5 and 6. The major components of this system were (1) the hydrogen and CO_2 gas stores composed of two cylindrical tanks complete with gauges, regulators and valves; (2) two gas drying columns containing $CaSO_4$; (3) two rotameters for precise metering of the hydrogen and CO_2 gas flow ratio; (4) the reactor containing the catalyst; (5) the water condensation coil and collection device, and (6) a Weston potentiometer for thermocouple temperature recording.
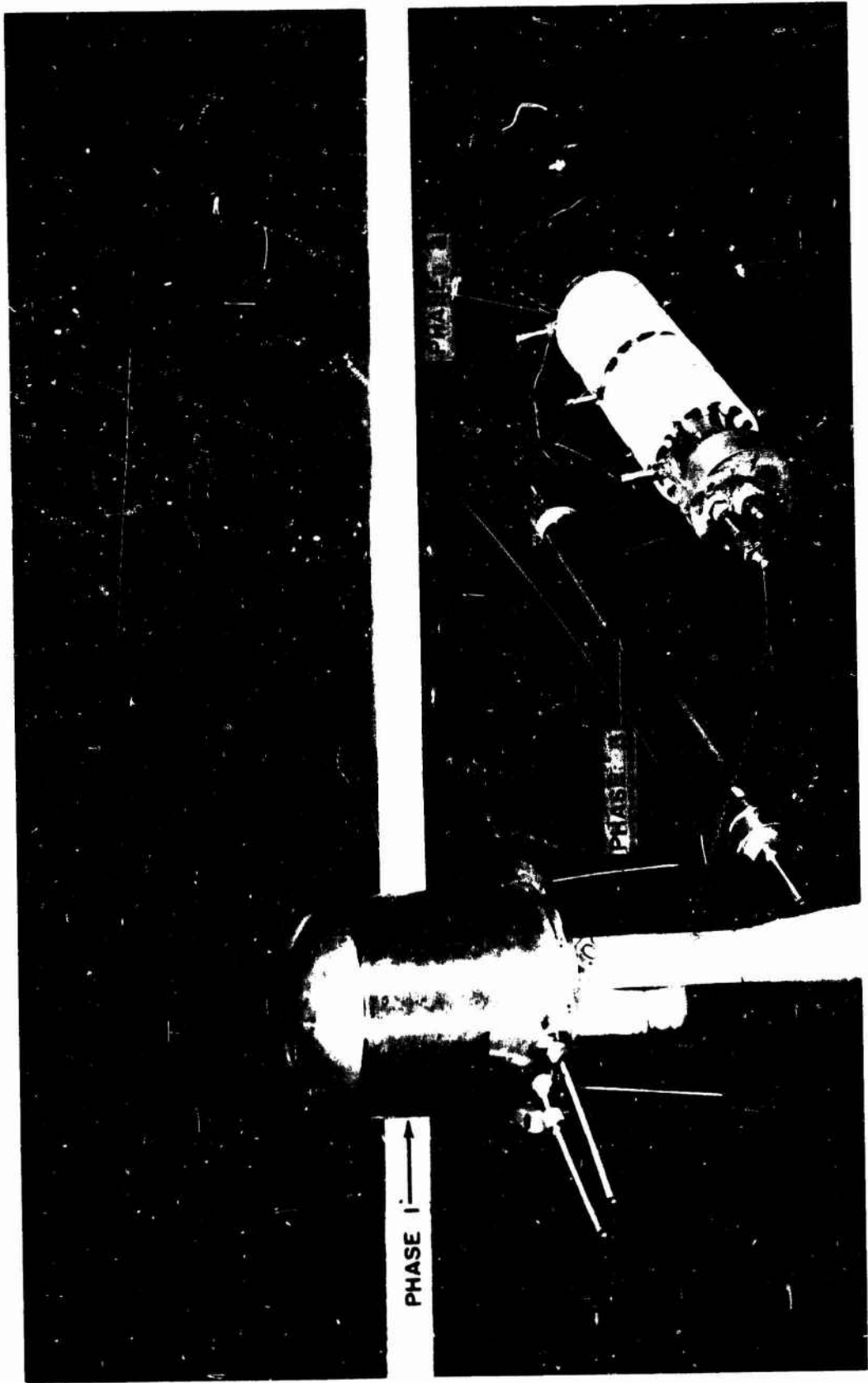
FDL-TDR-64-22, Part III

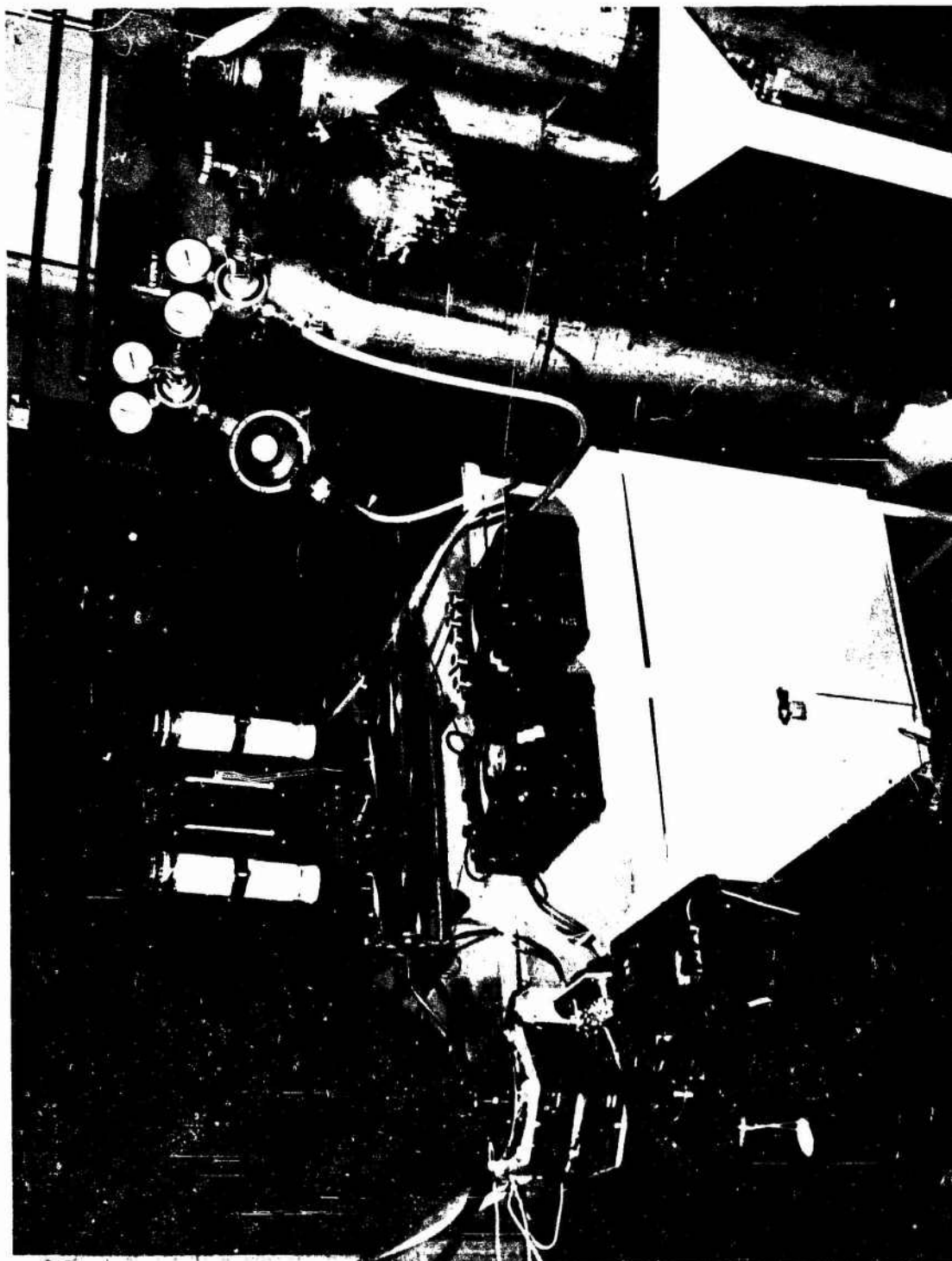Figure 4. Catalytic Reactors

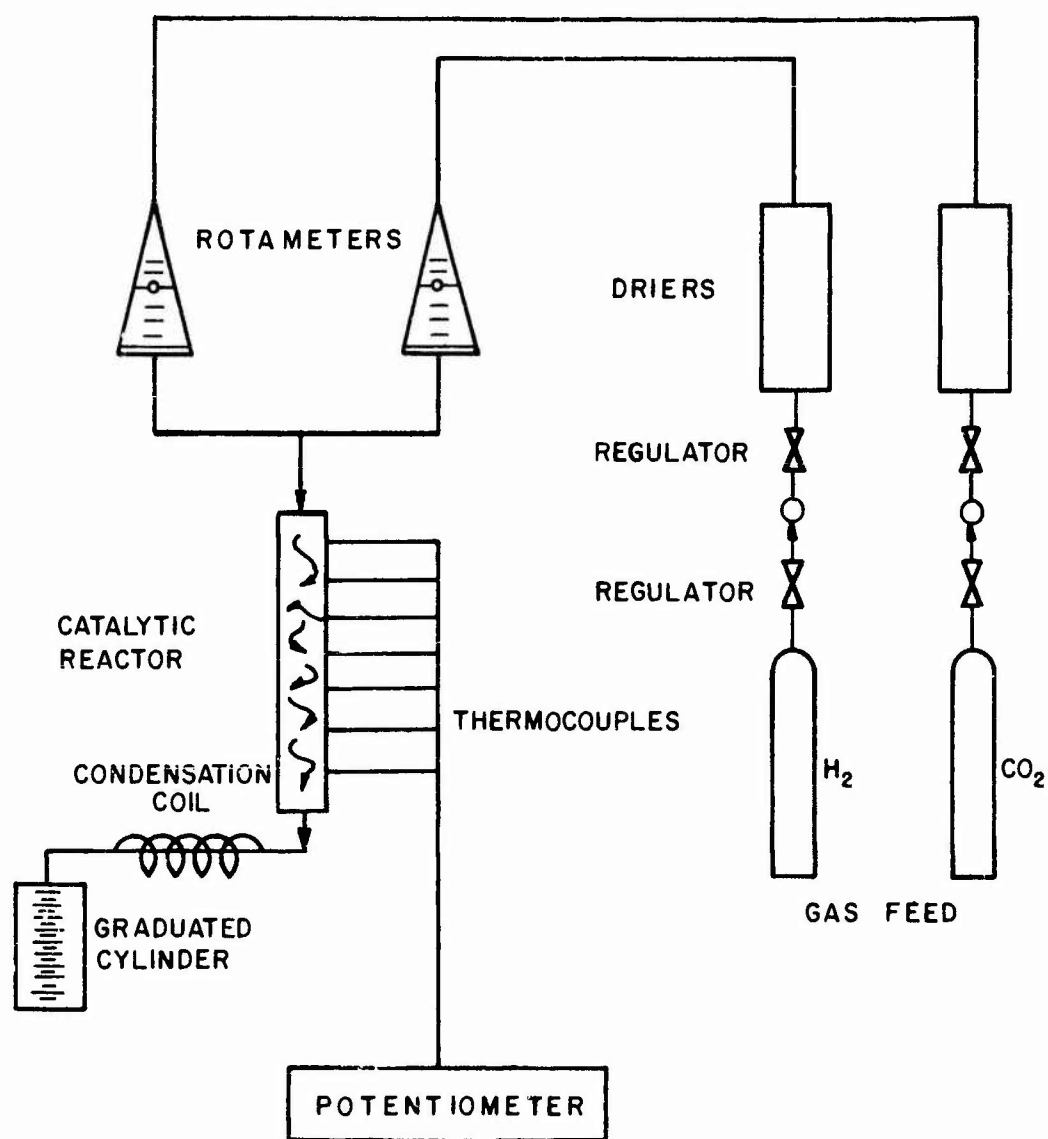18

Figure 5. CO_2 Reduction System
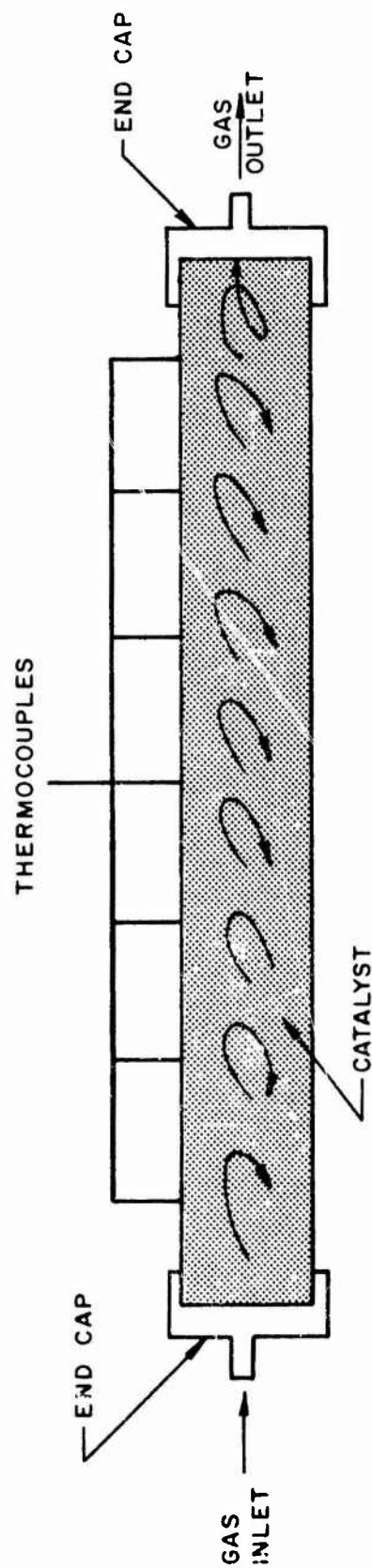
Figure 6. CO_2 Reduction System Flow Diagram

Figure 7. Catalytic Reactor Flow Diagram

The catalytic reactor, shown diagramatically in Figure 7, consists of a stainless steel cylinder 2.54 cm inside diameter and 48 cm long. The outer wall of the reactor was insulated with an asbestos cloth. The hydrogen and CO_2 gases enter at one end of the reactor and diffuse over the catalyst to the opposite end which serves as the exit port. This reactor, designated reactor No. 3, is unique in that it does not contain a gas flow reverser or a counterflow heat exchanger, characteristic of reactors 1 and 2 used in phases 1 and 2. These were eliminated so that the effect of the reaction exotherm (41 Kcal/mole CO_2 converted) on the temperature of the catalyst bed could be determined while the reaction was in progress. The catalytic reactor wall was fabricated for the implacement of seven iron-constantan thermocouples installed at equal intervals along the longitudinal wall of the reactor. The weight of the reactor batch loadings of the three catalysts of ruthenium, rhodium, and iridium were 257.5 g, 255.8 g, and 252.6 g, respectively. Each catalyst consisted of cylindrical pellets of 0.32 cm long and 0.32 cm in diameter. The catalyst bed was heated through the outer wall by a cylindrically wound nichrome wire resistance heater. The nichrome wire was separated by insulation from the reactor wall by approximately 0.25 cm. The nichrome resistance heater required 290 watts at 57.5 volts,5.05 amps to heat the catalyst bed in 35 minutes to the designated maximum reaction temperature of 900°F.

The water condenser consisted of a cylindrically wound copper tubing coil (8 inches long and 6 inches in diameter) and a graduated cylinder of 100 ml capacity. Water vapor leaving the reactor was condensed in the coil and collected in the graduated cylinder, thus providing direct measurement of yield. The products were not recycled through the reactor and therefore the apparatus did not include a recycling pump.

Two Brooks-Perkins gas flow rotameters were used to meter the H_2 and CO_2 gases to the reactor inlet manifold. The rotameter for hydrogen flow measurement (Brooks Model 1110) has a stainless steel ball float for metering hydrogen in a range of 200 to 2800 cc/min; specific gravity at 0.069, gas temperature and pressure at 70°F and 4 psig. The tolerance of accuracy is ± 2 percent of maximum flow. The rotameter for CO_2 flow measurement (Brooks Model 1110) has a sapphire float for metering CO_2 in a range of 50 to 500 cc/min, specific gravity at 1.529, gas temperature and pressure at 70°F and 4 psig. The tolerance of accuracy is also ± 2 percent of maximum flow.

The feed gases of H_2 and CO_2 were stored in two separate cylindrical tanks and metered individually through high pressure regulators to a lower pressure of 4 psig. The pressure level of 4 psig was maintained with precise accuracy since both rotameters were calibrated for this pressure and the flow rate is a direct indication of the CO_2 reduction rate. The high pressure regulators were also equipped with feed throttle valves for manual adjustment of the feed flow rates to meet the H_2/CO_2 flow rate ratio requirement set for any particular experiment. Two desiccator drying columns containing $CaSO_4$ were installed in parallel in both outlet lines from the high pressure regulators to remove any residual water vapor in the gas feed lines.

The potentiometer has two scales, one for low temperature readings in the range of 0 to 1000°F, and the second for high temperature readings in the range of 1000° to 2000°F. The tolerance of accuracy on the low and high ranges is 0.5 and 0.1 percent, respectively. Since the catalyst bed temperatures encountered in this experimental program were on the order of 300° to 900°F, a practical tolerance of 0.3 percent can be assumed. The iron-constantan thermocouple was used instead of copper-constantan because of its high reliability for readings in the medium temperature range.

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EXPERIMENTS

Results - Ruthenium

Twelve experimental reaction runs of two hours duration were conducted for the ruthenium on alumina catalyst, each run representing a different preheated reactor temperature. The initial run was made at 350°F with a corresponding reaction yield of 5 percent. Each of the additional eleven runs were made at 50°F high increments, the last run taking place at a temperature of 900°F. The maximum water percentage conversion of CO_2 occurred at the minimum temperature of 447°F. The next five runs showed essentially the same percentage conversion. The last five runs from 700° to 900°F showed progressively decreasing percentage conversion.

The hydrogen CO_2 flow rate ratio was maintained at 4.35 for all the experimental runs. This ratio had been determined in phases 1 and 2. The hydrogen gas flow rate was 1850 cc/min, and the CO_2 gas flow rate was 425 cc/min. The gases were metered from storage at 4 psig and "dried" in the $CaSO_4$ desiccator columns prior to entering the reactor.

During the experimental runs it was indicated that thermocouple No. 6 nearest the exit port to the reactor had malfunctioned and was not recording a temperature commensurate with the readings obtained from the other six thermocouples. It was decided to reply on the temperature indicated by the middle thermocouple or thermocouple No. 4 for a "true" catalyst bed temperature reading. The temperature shown by this thermocouple was always the highest reading obtained for the seven thermocouples. (See Figure 8.)
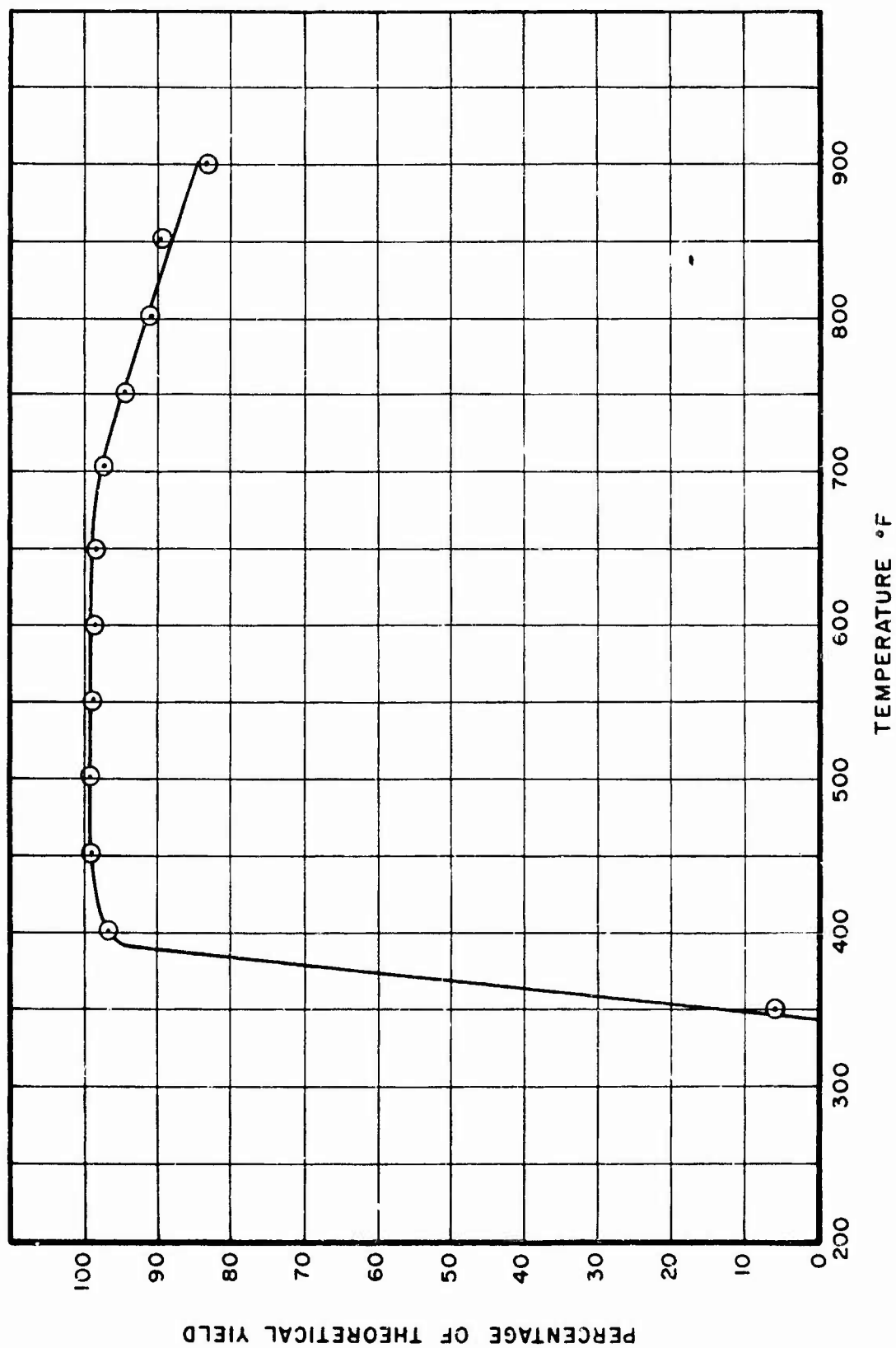
Figure 8. Sabatier Reaction – Percentage of Theoretical Yield
vs. Temperature for Ruthenium

The catalyst pellets were inspected at the completion of each experimental run. There was evidence of slight carbon deposition on the pellets after the runs conducted at 850° and 900°F.

Results - Rhodium

Twelve experimental reaction runs each of two hours duration were conducted with the 0.5 percent rhodium on alumina catalyst. The hydrogen/CO_2 flow rate ratio was kept at 4.35 stoichiometric reactant conditions. The first run was made at a temperature of 350°F and the succeeding runs were made at 50°F higher increments. The hydrogen gas flow rate was held at 425 cc/min for all experiments.

The gases were metered from storage at 4 psig and "dried" in the $CaSO_4$ desiccator columns prior to entering the reactor. The maximum water percentage conversion of CO_2, 99 percent, occurred at the minimum temperature of 704°F. Two additional runs at 750° and 800°F produced the same percentage conversion. The experimental runs taking place at 850° and 900° F showed decreased percentage conversion.

Thermocouple No. 6 also failed to operate correctly during these experimental runs to evaluate the rhodium catalyst and so its readout was disregarded. The other six thermocouples, particularly thermocouple No. 4, were used for temperature recording.

Inspection of the catalyst pellets after each experimental run indicated no degradation or partial reduction of the rhodium catalyst. (See Figure 9.)
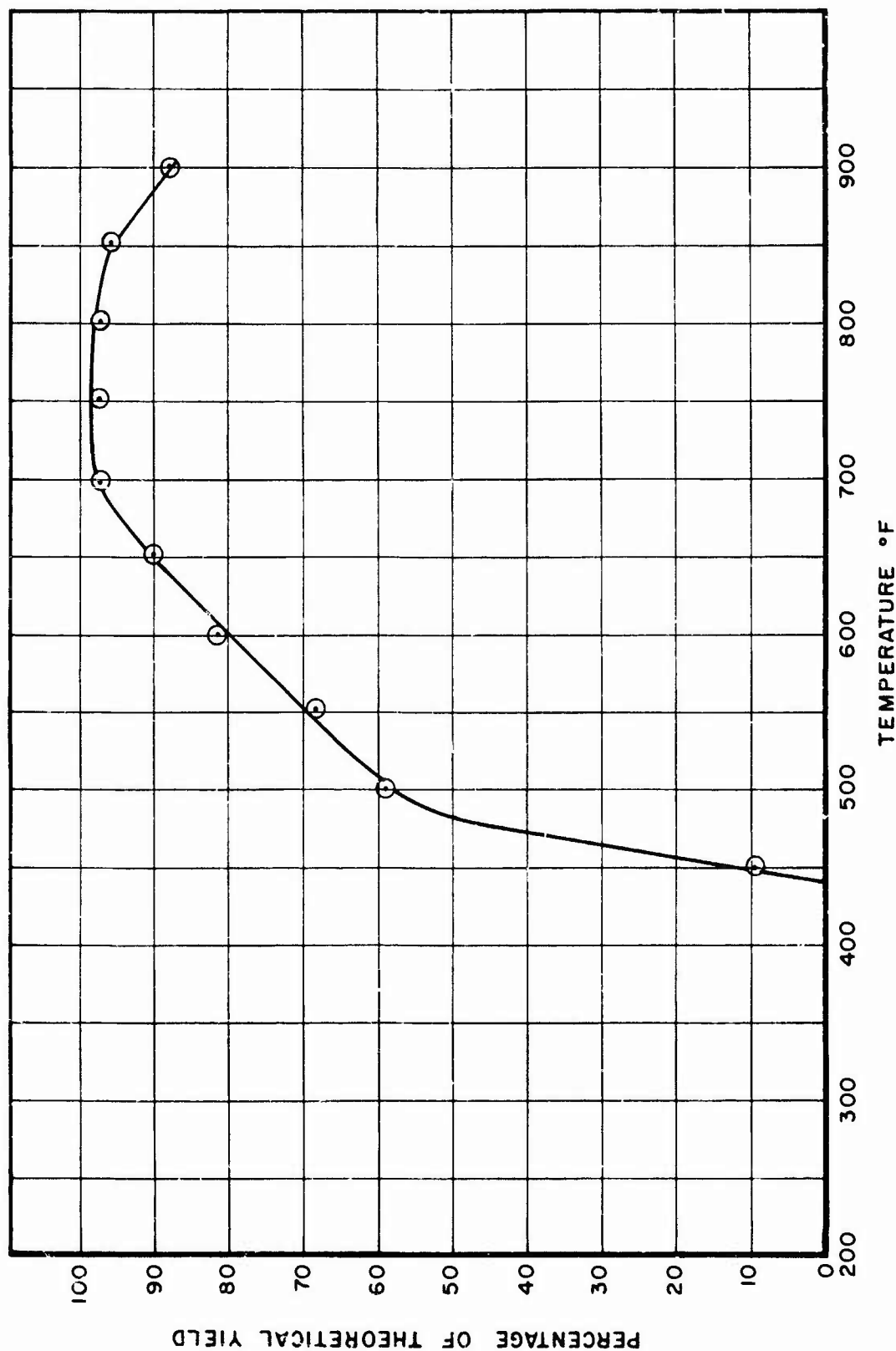
Figure 9. Sabatier Reaction – Percentage of Theoretical Yield vs. Temperature for Rhodium

Results - Iridium

Twelve experimental reaction runs, each of two hours duration were conducted with the 0.5 percent iridium on alumina catalyst. The hydrogen/CO_2 flow rate ratio was kept at 4.35, stochiometric reactant conditions. The first run was made at a temperature of 350°F and each succeeding run was made at 50°F higher increments. The hydrogen gas flow rate was maintained at 1850 cc/min; the CO_2 gas flow rate was held at 425 cc/min for all experimental runs.

The gases were metered from storage at 4 psig and "dried" in the $CaSO_4$ desiccator column prior to entering the reactor. The maximum water percentage conversion of CO_2, 67 percent, occurred at the minimum temperature of 892°F. The iridium catalyst did not effect the reduction reaction until a temperature of 600°F was exceeded. After the temperature of the catalyst bed was increased the percentage conversion increased almost linearly.

Thermocouple No. 6 was disregarded for temperature recording. The iridium catalyst was inspected after each run and showed partial reduction at the higher reaction temperatures. (See Figure 10.)
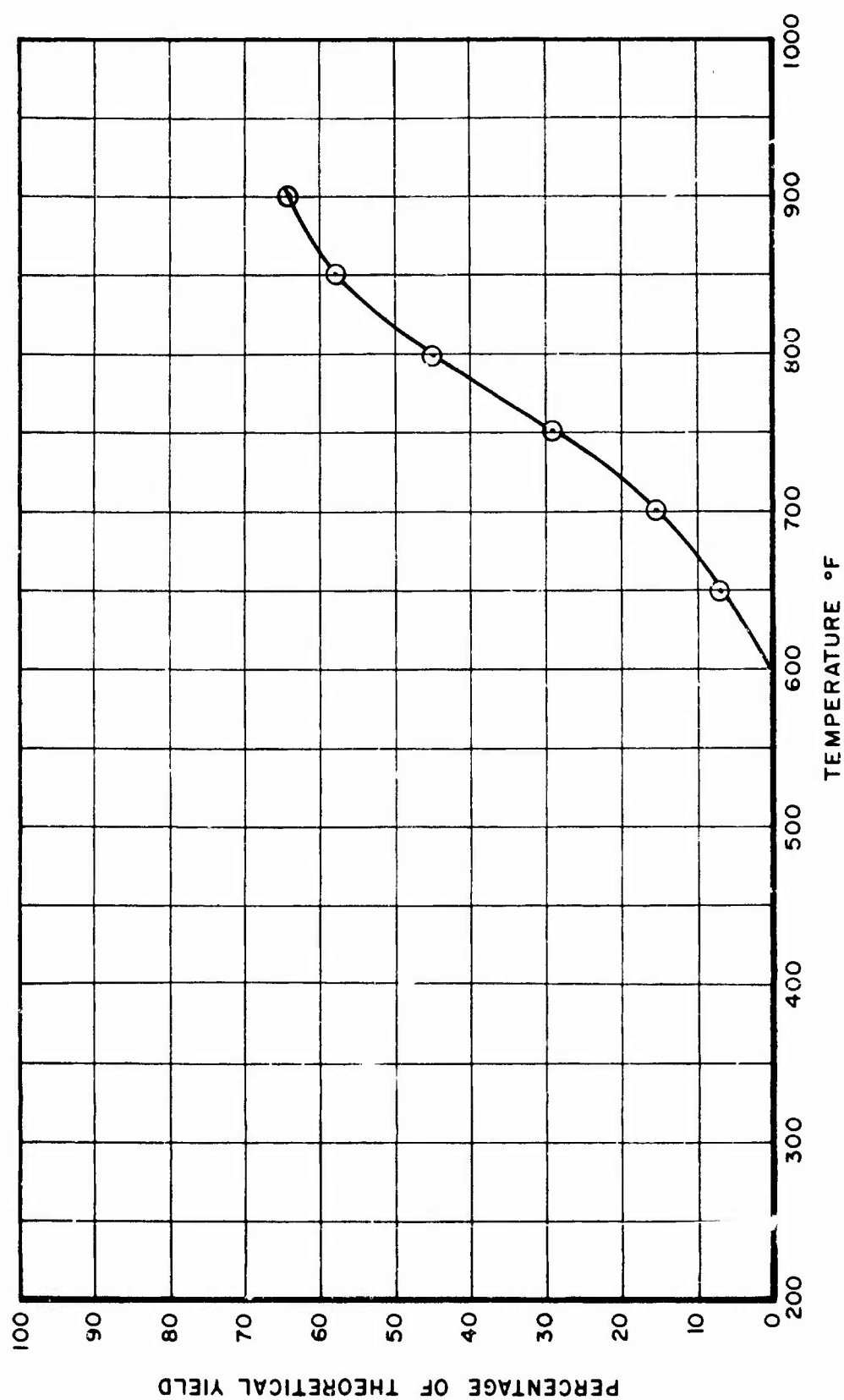
Figure 10. Sabatier Reaction - Percentage of Theoretical Yield
vs. Temperature for Iridium

TABULATION OF EXPERIMENTS
RUTHENIUM

EXPERIMENT	REACTOR TEMP (°F)	H_2 FLOW RATE (cc/min)	CO_2 FLOW RATE (cc/min)	H_2/CO_2 FLOW RATE RATIO	SPACE VELOCITY (hr^{-1})	WATER YIELD (cc)
1	350	1850	425	4.35	589	4
2	400	1850	425	4.35	589	61
3	450	1850	425	4.35	589	65
4	500	1850	425	4.35	589	65
5	550	1850	425	4.35	589	65
6	600	1850	425	4.35	589	65
7	650	1850	425	4.35	589	65
8	700	1850	425	4.35	589	63
9	750	1850	425	4.35	589	61
10	800	1850	425	4.35	589	59
11	850	1850	425	4.35	589	57
12	900	1850	425	4.35	589	54

TABULATION OF EXPERIMENTS
RHODIUM

EXPERIMENTS	REACTOR TEMP (°F)	H_2 FLOW RATE (cc/min)	CO_2 FLOW RATE (cc/min)	H_2/CO_2 FLOW RATE RATIO	(hr^{-1}) SPACE VELOCITY	WATER YIELD (cc)
1	350	1850	425	4.35	589	None
2	400	1850	425	4.35	589	None
3	450	1850	425	4.35	589	7
4	500	1350	425	4.35	589	38
5	550	1850	425	4.35	589	45
6	600	1850	425	4.35	589	53
7	650	1850	425	4.35	589	59
8	700	1850	425	4.35	589	63
9	750	1850	425	4.35	589	64
10	800	1850	425	4.35	589	64
11	850	1850	425	4.35	589	62
12	900	1850	425	4.35	589	57

TABULATION OF EXPERIMENTS
IRIDIUM

EXPERIMENT	REACTOR TEMP (°F)	H_2 FLOW RATE (cc/min)	CO_2 FLOW RATE (cc/min)	H_2/CO_2 FLOW RATE RATIO	SPACE VELOCITY	WATER YIELD (cc)
1	350	1850	425	4.35	589	None
2	400	1850	425	4.35	589	None
3	450	1850	425	4.35	589	None
4	500	1850	425	4.35	589	None
5	550	1850	425	4.35	589	None
6	600	1850	425	4.35	589	None
7	650	1850	425	4.35	589	5
8	700	1850	425	4.35	589	10
9	750	1850	425	4.35	589	19
10	800	1850	425	4.35	589	29
11	850	1850	425	4.35	589	38
12	900	1850	425	4.35	589	42

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The overall conclusion reached from the combined investigations of phases 1, 2, and 3 is that the preferred catalyst for effecting the low temperature reduction of carbon dioxide to methane and water is 0.5 percent ruthenium on alumina. This catalyst, investigated and discussed in this report, demonstrated its superiority to the nickel-kieselguhr catalyst evaluated during phase 1. The ruthenium on alumina catalyst, or possibly ruthenium metal granules, would be the choice catalyst at this time for application to oxygen recovery systems for spacecraft.

Specific conclusions reached during the phase 3 investigation are as follows:

(a) Ruthenium on alumina is the most effective catalyst of all those investigated for promoting the Sabatier reaction.

(b) The conversion rate of 99 percent can be obtained using the ruthenium catalyst in a single pass reactor. An excess of catalyst must be used for a reactor space velocity of 550 hr^{-1}

(c) The ruthenium catalyst does not require hydrogen purging for removal of residual poisons in the reactor operating temperature range of 350° to 500°F.

(d) Iridium is virtually ineffective as a low temperature CO_2 reduction catalyst. This catalyst also shows substantial degradation of properties at temperatures above 600°F.

(e) All accessory equipment and instrumentation functioned perfectly during the experimental program.

(f) The catalytic reactor designated reactor No. 3 functioned perfectly during the program.

(g) Reactor No. 3 has a length to diameter ratio of 18 and exhibits a wide temperature variation of as much as 180°F between the seven thermocouples installed in the reactor.

RECOMMENDATIONS

The following recommendations are made for consideration in future investigations.

(a) The ruthenium and rhodium catalysts should be investigated for catalytic effectiveness in reactors of varying lengths/diameter ratios. Consideration should also be given to varying the size and shape of the catalyst pellets.

(b) The inhibiting effect of common catalyst poisons such as the gaseous sulfides and halogens on the effectiveness of ruthenium and rhodium catalysts should be determined.

(c) Long duration continuous experimental runs up to several days should be conducted to determine possible degradative effects on the catalysts.

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13. ABSTRACT

The precious metals of ruthenium, rhodium, and iridium were selected as the final group of catalyzing materials to be experimentally evaluated for effectiveness in promoting the catalytic reduction of carbon dioxide by hydrogen to methane and water. A catalytic reactor having a length to diameter ratio of 18 was designed, fabricated, and utilized for the experimental evaluation of these catalysts. The reactor processed 2.2 pounds of CO_2 per day equivalent to a one-man daily output. The minimum temperature required to achieve the maximum CO_2 conversion rate of 99 percent was 450 F and this occurred for the ruthenium catalyst. Conversion rates of 99 and 67 percent were obtained with the rhodium and iridium catalysts at temperatures 704° and 892° F, respectively. The 99 percent conversion rate for ruthenium held for the temperature range of 450° to 650° F. All reactions took place at 1 atmosphere pressure. The total weight of hydrogen required to reduce the 2.20 pounds of CO_2 under these conditions is 0.39 pounds. Each of the three catalysts had reactor batch weights of approximately 253 to 258 grams. After completion of each experimental run at the pre-set temperature, the catalyst was examined for possible carbon deposition and physical deterioration. No evidence of either condition was noted for ruthenium and rhodium: the iridium catalyst, however, had been partially reduced at the higher experimental reaction temperatures. The report introduces discussions of the effect of quantitative factors such as catalyst particle size and shape on reaction yield.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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